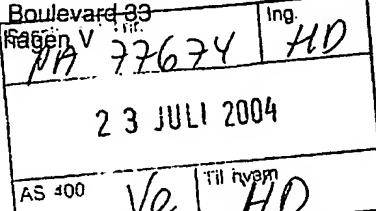
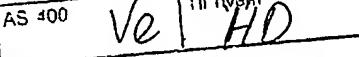


PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:
CHAS. HUDE A/S H.C. Andersens Boulevard 33 DK-1780 Copenhagen V DANEMARK
 23 JULI 2004 

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Applicant's or agent's file reference 77674 HDv	IMPORTANT NOTIFICATION	
International application No. PCT/DK 03/00497	International filing date (day/month/year) 15.07.2003	Priority date (day/month/year) 16.07.2002
Applicant DANMARKS TEKNISKE UNIVERSITET-DTU et al.		

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/I/B/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx. 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Marchetto, L Tel. +49 89 2399-2796
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PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

REC'D 22 JUL 2004

WIPO PCT

Applicant's or agent's file reference 77674 HD/ve	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/DK 03/00497	International filing date (day/month/year) 15.07.2003	Priority date (day/month/year) 16.07.2002
International Patent Classification (IPC) or both national classification and IPC C23C8/22		
Applicant DANMARKS TEKNISKE UNIVERSITET-DTU et al.		

<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 6 sheets.</p>	
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the opinion II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 	

Date of submission of the demand 12.02.2004	Date of completion of this report 21.07.2004
Name and mailing address of the International preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Mizera, E Telephone No. +49 89 2399-8580
	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/DK 03/00497**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

2, 5-11 as originally filed
1, 3, 4, 12 filed with telefax on 09.07.2004

Claims, Numbers

1-9 filed with telefax on 09.07.2004

Drawings, Sheets

1/2, 2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/DK 03/00497

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-9
	No: Claims	
Inventive step (IS)	Yes: Claims	1-9
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-9
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/DK 03/00497

1. The following documents are cited:

D1: NL-A-1 003 455 (RIJKSUNIVERSITEIT GRONINGEN TE GRONINGEN) 2 March 1998 (1998-03-02)

D2: US-A-4 013 487 (RAMQVIST LARS H ET AL) 22 March 1977 (1977-03-22)

D3: DATABASE WPI Section Ch, Week 198408 Derwent Publications Ltd., London, GB; Class M13, AN 1984-045734 XP002262970 & JP 59 006367 A (NICCHI KK) 13 January 1984 (1984-01-13)

D4: EP-B-0 248 431 (POLITECHNIKA KRAKOWSKA ;SAMOCHODOW MALOLITRAZOWYCH POL (PL)) 9 December 1987 (1987-12-09)

D5: DD 294 048 A (FREIBERG BERGAKADEMIE) 19 September 1991 (1991-09-19)

D6: WO 01/55470 A (MARX STEVEN V ;SWAGELOK CO (US); WILLIAMS PETER C (US)) 2 August 2001 (2001-08-02)

D7: WO 00/50661 A (MARX STEVEN V ;SWAGELOK CO (US); WILLIAMS PETER C (US)) 31 August 2000 (2000-08-31)

2. None of the prior art documents D1-D7 discloses a method of hardening a stainless steel article comprising a top layer which includes metal from the group Ni, Ru, Co and Pd. D1-D3 do not disclose stainless steel articles, whereas D4 to D7 are directed to articles comprising a top layer of Fe.

3. Claims 1-9 are thus novel under Art.33(2) PCT.

4. The beneficial effects of a top layer from a metal of the group defined in claim 1 compared to a top layer of Fe can be derived from Example 7 (see in particular p.10, l.27 to p.11, l.14). Obviously a more noble material is obtained after nitriding when using e.g. Ni as compared to Fe.

5. D2 suggests working in a temperature range of 800-1000 °C, which would result in the formation of chromium carbides. D3 discloses a low alloy steel article with only 1.12 % Cr. Such articles cannot be regarded as stainless steel articles. In D1 the formation of a nitride layer is explicitly mentioned. Moreover case hardening of iron and low-alloyed steel, but not of stainless steel is disclosed in this document.

6. Claim 1 is not rendered obvious by the cited prior art so that the requirements of Art.33(3) EPC are met. This applies also to claims 2-9, depending on this claim.

Title: Case-hardening of stainless steelTechnical Field

5 The present invention relates to a method according to the preamble of claim 1.

Background Art

Thermo-chemical surface treatments of steel by means of carbon or nitrogen carrying gases are well-known processes, called case-hardening or carburization or nitriding. Nitro-carburization is a process in which a gas carrying both carbon and nitrogen is used. These processes are traditionally applied to improve the hardness and wear resistance of iron and low alloyed steel articles. The steel article is exposed to a carbon and/or nitrogen carrying gas at an elevated temperature for a period of time, 15 whereby the gas decomposes and carbon and/or nitrogen atoms diffuse through the steel surface into the steel material. The outermost material close to the surface is transformed into a layer with improved hardness, and the thickness of this layer depends on the treatment temperature and the treatment time.

20 Stainless steel has excellent corrosion properties, but is relatively soft and has poor wear resistance, especially against adhesive wear. Therefore, there is a need of improving the surface properties for stainless steel. Gas carburization, nitriding and nitro-carburizing of stainless steel involve some difficulties, as the passive layer, causing the good corrosion properties, acts as a barrier layer preventing carbon and/or nitrogen atoms from diffusing through the surface. Also the elevated temperatures of the treatments promote the formation of chromium carbides or chromium nitrides. 25 The formation of chromium carbides and/or chromium nitrides reduces the free chromium content in the material whereby the corrosion properties are deteriorated.

process can be carried out at temperatures below 400°C, and the purpose is to obtain a pore-free iron nitride layer.

Disclosure of Invention

5

The object of the invention is to provide a new and improved method for case-hardening stainless steel. The object of the invention is obtained by a process according to the preamble of claim 1, wherein the top layer includes metal which is catalytic to the decomposition of the gas carrying the carbon or/and nitrogen atoms and which is one or more of the metals Ni, Ru, Co or Pd. The metal layer protects the stainless steel surface from oxidation and acts as a catalytic surface for the decomposition of the gas. As a result, the process temperature can be kept below the temperature at which carbides and/or nitrides are formed, and the process can be finished within a reasonable period of time. After the thermo-chemical treatment, the catalytic metal layer can be removed to expose and repassivate the hardened stainless steel surface.

When carbon atoms, nitrogen atoms or both diffuse into stainless steel, the metastable S-phase is formed. S-phase is also called "expanded austenite" and has carbon and/or nitrogen in a solid solution at an upper stable temperature of about 450°C when it is nitrogen-stabilized, and at about 550°C when it is carbon-stabilized. Thus, the process according to the invention can be carried out at temperatures up to 450°C or 550°C to obtain S-phase.

25 Until now, S-phase in stainless steel has almost only been obtained by plasma-assisted or ion implantation-based processes. Tests have established that the formation of S-phase at the surface does not negatively change the corrosion resistance of stainless steel. For nitrogen-stabilized S-phase an improvement of corrosion resistance can be obtained.

30

When stainless steel is treated with the method according to the invention, the hardness and wear resistance are improved considerably without the deterioration of the corrosion properties.

5 The ammonia synthesis, i.e. the production of NH_3 from H_2 and N_2 , involves the use of a number of catalytic metals. Traditionally, the process is carried out at temperatures in the range $400^\circ\text{C} - 700^\circ\text{C}$ at high pressures (>300 atm) in the presence of a catalyst material. Gaseous nitriding is in principle the reverse process of the ammonia synthesis, where ammonia is dissociated on a metal surface producing N available for diffusion into the material to be nitrided. The conventional nitriding process is carried out within the same temperature interval as the ammonia synthesis process but at normal pressures. The catalytic metals available in the ammonia synthesis process are also found to promote the low-temperature catalytic reaction (ammonia dissociation) of the nitriding process. Known catalysts from the ammonia synthesis process include Fe, Ni, Ru, Co, Pd among others.

According to an embodiment of the invention, the case-hardening is a nitriding process which is carried out with a nitrogen containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C .

20

EP 0248431 B1 discloses a method where an austenitic stainless steel article is electroplated with iron before nitriding at 575°C for 2 hours. As mentioned before, chromium nitrides are formed at this temperature. As disclosed on page 4, lines 13 to 18 of EP 0248431 B1, only the valve shaft of a valve is nitrided. The valve disk (Ventilteller) is protected from nitriding by an oxide layer in order not to reduce the corrosion resistance of the valve disk.

The same idea is followed with respect to carburizing, where the same catalytic metals are applicable also.

- 5 The material applied for the surface layer should include the well known materials from the ammonia synthesis process either as pure metals (single layer), as alloys, as a metal layer doped with other metals and as multi-layers.

Claims

1. A method of case-hardening a stainless steel article by means of gas including carbon and/or nitrogen, whereby carbon and/or nitrogen atoms diffuse through the surface of the article, the case-hardening is carried out below a temperature at which carbides and/or nitrides are produced, the method including activating the surface of the article, applying a top layer on the activated surface to prevent repassivation, the top layer includes metal which is catalytic to the decomposition of the gas, characterised in that the metal is one or more of the metals Ni, Ru, Co or Pd.
- 10 2. A method according to claim 1, wherein the case-hardening is a nitriding process which is carried out with a nitrogen-containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C.
- 15 3. A method according to claim 1, wherein the case-hardening is carburizing with a carbon-containing gas, preferably CO.
4. A method according to claim 3, wherein carburizing is carried out below a temperature at which carbides are produced, preferably below approximately 550°C, more preferably below approximately 510°C.
- 20 5. A method according to any of the preceding claims, wherein the top layer is a nickel layer.
- 25 6. A method according to claim 5, wherein the maximum average thickness of the nickel layer is 300 nanometer, preferably 200 nanometer.
7. A method according to claim 5 or 6, wherein the nickel layer is applied by a chemical or electrolytical plating process, e.g. by electro-plating in a Wood's nickel
- 30 bath.

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NO. 4596 P. 10

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Amended claims of 9 July 2004

8. A method according to any of the preceding claims, wherein the article is of austenitic stainless steel.
9. A method according to any of the preceding claims, wherein the catalytic metal layer is only applied to parts of the surface of the stainless steel article.